

Linear Aggregation Revisited: Rods, Rings and Worms

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Abstract. – The problem of ring formation in solutions of cylindrical micelles is reinvestigated theoretically, taking into account a finite bending rigidity of the self-assembled linear objects. Transitions between three regimes are found when the scission energy is sufficiently large. At very low densities only spherical and very short, rod-like micelles form. Beyond a critical density, mainly rings but also rod-like chains appear in (virtually) fixed relative amounts. Above a second transition both the length of the linear chains and the relative amount of material taken up by them increase rapidly with increasing concentration. The mass accumulated into long, semi-flexible worms then overwhelms that in rings. The ring-dominated regime is very narrow for semi-flexible chains, confirming that the presence of rings may be difficult to observe in many micellar systems, and indeed disappears completely for sufficiently low scission energy and/or large persistence length.

Solutions of highly elongated, cylindrical micelles are arguably among the best studied of the so-called equilibrium polymeric systems [1]. Equilibrium polymers are formed in a reversible polymerisation process and therefore are in chemical equilibrium with each other – monomeric material is continually exchanged between the assemblies. An aspect not at all well understood is why ring closure seems to be unimportant in solutions of linear micelles, although this would remove unfavourable free ends (“end caps”) from the solution. (Closed loops have been observed in electron microscopic images of linear micelles [2], but apparently they occur in too low concentrations to significantly influence the properties of micellar systems [1].) In other equilibrium polymeric systems, such as liquid sulphur, the presence of rings is on the other hand thought to be all-important [3]. According to mean-field theory [3], rings must indeed overwhelmingly dominate the aggregate population in solutions of self-assembled, *flexible* polymers, but only when the monomer fugacity is below some threshold value. At

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fugacities above this threshold, the concentration of rings should level off to a constant value. Linear chains then form an increasingly important fraction of the aggregated material. In the limit where the end caps carry an infinite free energy penalty, the crossover becomes sharp and is reminiscent of a phase transition, sometimes referred to as the polymerisation transition [3].

Ignoring the subtle effects of excluded volume interactions which give rise to departure from mean-field behaviour [3, 4, 5, 6], the self-assembled linear chains behave as if the rings were not present above the polymerisation transition, although the rings do deplete a fixed amount of material available to linear aggregation [7]. The amount of material incorporated into rings is then roughly equal to the volume fraction at the polymerisation threshold which, for flexible aggregates, is predicted to take place at an estimated value of the order ten per cent. This is at variance with experimental observations on micellar solutions, where in some cases giant, polymer-like assemblies are known to arise at volume fractions as low as one tenth of a per cent [1]. Some workers have conjectured that a *finite bending rigidity* of the micelles could suppress rings smaller than a certain size, thereby reducing the contribution of rings [4]. Others argued that the formation of rings is anyway more strongly attenuated than any estimate based on a Gaussian bead-spring model can predict. This is essentially because the number of places a continuous ring can break is much greater than that of a discrete ring [7]. Although both views are not entirely inaccurate, we shall see below that the issue is decidedly more complex and worth of study.

In this Letter, we reinvestigate linear self-assembly in three spatial dimensions by explicitly taking into account the finite bending rigidity of the chains. We find three regimes, one where spherical and possibly also short, rod-like aggregates are overwhelmingly present, one where closed rings constitute a significant if not dominant portion of the micelle population, and one where long, worm-like assemblies emerge to become the dominant species, see figure 1. For semi-flexible linear assemblies containing many monomers per persistence length, the crossovers between the various regimes occur at such low volume fractions that for most practical purposes ring formation can be ignored. This explains experimental observation, and is in line with an earlier (less elaborate) analysis of Porte [7]. We also find conditions under which the ring phase disappears altogether.

We consider a micellar solution above the critical micelle concentration, cmc. We assume that at (or slightly above) the cmc the micelles are essentially spherical, and that we can disregard the presumably constant amount of the dissolved surfactant not incorporated into micelles. In our model, the spherical micelles are viewed as the basic monomeric units that self-assemble into elongated, continuous chains. Whether in actual fact single surfactant molecules self-assemble into cylinders or whole groups of surfactants is inessential to the theory. The cylindrical assemblies can be open (linear) or closed (circular), and are assumed to be semi-flexible. This implies that the length each “monomer” contributes to the total length is considerably smaller than the persistence length. Self-interactions of the excluded volume type are comparatively weak in solutions of semi-flexible chains [8], so the chains may be treated as ideal. The dimensionless number density of assemblies of aggregation number N is denoted $\rho(N)$, where the subscripts 0 and 1 shall be used to refer to closed rings and linear chains, respectively. Balancing the loss of translational entropy of a monomer when incorporated into an aggregate against the free energy gain of association immediately gives, in the mean field, $\rho(N) = Z(N) \exp(\tilde{\mu}N)$ for the equilibrium size distribution. The chain partition function $Z(N > 1)$ depends on the topology of the aggregate as well as on the prevailing flexibility mechanism. We take as a reference the “internal” partition function of a free monomer, and define $Z(1) \equiv 1$. The (dimensionless) chemical potential of the monomers, $\tilde{\mu}$, can be related to the total volume fraction of aggregating material, ϕ , via the normalisation condition $\phi = \phi_0 + \phi_1$, where $\phi_0 \equiv \sum_{N=2}^{\infty} N \rho_0(N)$ and $\phi_1 \equiv \sum_{N=1}^{\infty} N \rho_1(N)$. In our calculations below,

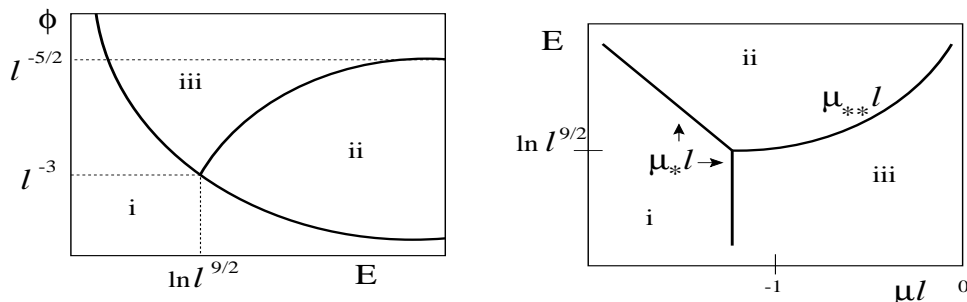


Fig. 1. – Schematic diagram of the aggregation states of semi-flexible micelles. Volume fraction ϕ vs the scission energy E . (i) Monomeric phase (spherical micelles), (ii) ring phase consisting mainly of rings and a few rods, both about a persistence length long, (iii) worm phase of long, worm-like aggregates, many persistence lengths long, and a few relatively short rings. Here l is a dimensionless persistence length and unimportant prefactors of order unity have been left out.

Fig. 2. – As figure 1, now given as a function of the scission energy E , and the chemical potential μ times the dimensionless persistence length l . Indicated are also the cross-over chemical potentials μ_* and μ_{**} , discussed in the main text.

we replace summations by integrations whenever the mean aggregation numbers are large, that is, whenever $\langle N \rangle_0 \equiv \phi_0 / \sum_{N=2}^{\infty} \rho_0(N) \gg 1$ and/or $\langle N \rangle_1 \equiv \phi_1 / \sum_{N=1}^{\infty} \rho_1(N) \gg 1$.

Given that the size distribution is directly proportional to the partition function Z , one would next like to obtain accurate expressions for the partition functions Z_0 and Z_1 for arbitrary aggregation numbers N . Within the rigid Gaussian chain model of semi-flexible linear chains, discussed recently by Marques and Fredrickson [9], the latter can be evaluated exactly in the entire range from the rod to the worm limit. We only quote the limiting results for the rod and worm limits, which can be expressed as $Z_1(N) \sim z^{N-1}((N-1)/l)^{3(N-2)/2}$ and $Z_1(N) \sim z^{N-1}(2l)^{-3/2}$ in these two limits $l \gg N \geq 2$ and $N \gg l$. Here $l \gg 1$ denotes the average number of monomers per persistence length, presumed large, and $z \equiv \lambda_1 l^{-3/2} \exp(\tilde{E})$ is a function of l and \tilde{E} , with λ_1 a constant of order unity. A Boltzmann term associated with the (dimensionless) free energy cost of chain scission, $\tilde{E} > 0$, has been explicitly added, penalising the free ends of the open chains. For long, polymer-like micelles values of \tilde{E} up to about 20 ($k_B T$) are not uncommon [1], although scission energies as high as 38 ($k_B T$) have been reported in the literature [10]. Note i) that the free energy of a single chain, $-\ln Z$, is extensive in the number of monomers N in the chain, as it should, but ii) that there are logarithmic corrections near the rod limit. These corrections very strongly suppress rod-like aggregates considerably smaller than one persistence length yet consisting of more than a few aggregating units. (We shall come back to this later.) As $Z_1(N) \ll z^{N-1}(2l)^{-3/2}$ for $2 \ll N \ll l$, we simply set $Z_1(N) = 0$ for the entire range $2 \leq N < l$, and $Z_1(N) = z^{N-1}(2l)^{-3/2}$ for $N \geq l$. The free monomers are from now on understood to also include short, rod-like micelles a few micelle diameters long. This merely renormalises the chemical potential.

Exact results for the partition function of closed loops of arbitrary flexibility are, as far as we are aware, not available in the literature, although limiting expressions have been obtained within several model descriptions. The problem of ring closure in the tight bending limit was addressed by Shimada and Yamakawa at the level of the worm-like chain model [11]. Their

result can be written as $Z_0 \propto \exp(-2\pi^2 l/N)$, valid when $l \gg N \gg 1$. (Here we ignore additional non-exponential dependences on N/l for reasons of brevity.) In other words, tight rings are exponentially suppressed. Again, we arbitrarily set the cut-off at $N = l$, and put $Z_0 = 0$ for all $1 \leq N < l$. (There is obviously no monomeric ring.) In the opposite limit of long chains, $N \gg l \gg 1$, a simple scaling argument allows us to deduce the partition function of the closed configurations, Z_0 , from that of the linear chains, Z_1 . The argument is a slight modification of the one given by Porte [7] (and others [3, 4]) for the case of flexible chains, and hinges on a consideration of the ratio Z_1/Z_0 . The ratio Z_1/Z_0 is equal to the probability of opening a loop, which must be proportional to i) the number of places the ring can break, N , ii) the volume that two neighbouring segments can explore after being disconnected, proportional to $N^{3/2}l^{3/2}$ [7], iii) the increased angular phase volume of these new end segments, $l^{1/2}$, and iv) a Boltzmann weight, $\exp(\tilde{E})$, for the creation of the two end caps. Using the previously given expression for Z_1 , we find $Z_0 \sim \lambda_0 z^N N^{-5/2} l^{-2}$ for $N \gg l \gg 1$, with λ_0 an unknown constant presumably close to unity. (Pfeuty and co-workers [3] set $\lambda_0 = 0.1$ in their analysis of self-assembled, flexible chains.) We extrapolate this expression in our calculations down to $N = l$. Our estimate for $Z_0(N > l)$ is smaller by a factor of $l^{-1/2}$ than the previous estimate of Ref. [7], due to the reduced angular phase volume of the two ends upon ring closure, not taken into account in that work.

The size distributions we thus obtain are

$$\rho_0(N) \simeq \begin{cases} 0 & \text{if } 1 \leq N < l \\ \lambda_0 N^{-5/2} l^{-2} \exp(\mu N) & \text{if } N \geq l \end{cases} \quad (1)$$

for the rings, and

$$\rho_1(N) \simeq \begin{cases} z^{-1} \exp(\mu) & \text{if } N = 1 \\ 0 & \text{if } 2 \leq N < l \\ \exp(-E + \mu N) & \text{if } N \geq l \end{cases} \quad (2)$$

for the linear chains, where in both expressions we have absorbed a $\ln z$ in the chemical potential, $\mu \equiv \tilde{\mu} + \ln z$, and a constant into the scission energy, $E \equiv \tilde{E} - \ln(2^{3/2}/\lambda_1)$, which we regard as the actual, measurable scission energy. Using eqs (1) and (2), we evaluate the relative contributions of chains and rings to the total volume fraction material ϕ , and calculate their mean lengths $\langle N \rangle$. Careful inspection of the various contributions to

$$\phi_0 \simeq 2\lambda_0 l^{-5/2} \left(\exp(\mu l) - \sqrt{-\pi \mu l} \operatorname{erfc}(\sqrt{-\mu l}) \right) \quad (3)$$

and to

$$\phi_1 \simeq z^{-1} \exp(\mu) + l^2 \exp(\mu l - E) \left(\frac{1}{(\mu l)^2} - \frac{1}{\mu l} \right) \quad (4)$$

reveals that, depending on the dimensionless chemical potential $\mu \leq 0$, three regimes can be distinguished. See figures 1 and 2. When $E \gg \ln(l^{9/2}\lambda_0^{-1})$ we find, at a fixed scission energy E , transitions between all three regimes upon increasing the chemical potential:

(i) The **monomer-dominated** regime: $\mu < \mu_*$, where $\mu_* \simeq -l^{-1} \ln(\lambda_1 l^{1/2} + \lambda_0 \lambda_1 l^{-4} \times \exp(E))$. For volume fractions $\phi < \lambda_1^{-1} l^{3/2} \exp(-E)$, almost all of the material resides in “monomers” with $\langle N \rangle_1 = 1$, i.e., in spheres and (possibly) in very short rods.

(ii) The **ring-dominated** regime: $\mu_* < \mu < \mu_{**}$, where $\mu_{**} \simeq -l^{5/4} (2\lambda_0)^{-1/2} \exp(-E/2)$. When $\mu_* < \mu < -l^{-1}$, rings and chains of about a persistence length long occur in a ratio almost independent of the concentration, $\phi_1/\phi = 1 - (\phi_0/\phi) \simeq 1/(1 + \lambda_0 l^{-9/2} \exp(E))$. The mean lengths $\langle N \rangle_0 \simeq \langle N \rangle_1 \simeq l(1 - (\mu l)^{-1}) \gg 1$ increase only logarithmically with ϕ . When $-l^{-1} < \mu < \mu_{**}$ the mass fraction of worms grows with increasing chemical potential.

(iii) The **worm-dominated** regime: $\mu_{**} < \mu \leq 0$. The fraction of worms overwhelms the ring fraction when $\mu > \mu_{**}$, that is, when $\phi > 4\lambda_0 l^{-5/2}$. The volume fraction of material held in rings levels off to $\phi_0 \simeq 2\lambda_0 l^{-5/2}$, as does the mean size $\langle N \rangle_0 \simeq 3l$. We find, furthermore, that in this worm-dominated regime $\langle N \rangle_1 = l(\phi - \phi_0)^{1/2} \exp(E/2) \gg l$. This is consistent with Porte's result [7], except for the different scaling of ϕ_0 with l .

When $E < \ln(l^{9/2}\lambda_0^{-1})$, in other words when the micelles are sufficiently stiff for a fixed scission energy E , the ring phase disappears and we are left with a single transition from a “monomeric” solution of spherical and short, rod-like micelles to a worm-dominated regime. The cross-over takes place when $\mu > \mu_* \simeq -(\mu_* l)^{-1} \exp(-\mu_* l)$, which for all sensible values of l gives $-\mu_* l = O(1)$ independent of the scission energy. The corresponding cross-over volume fraction, however, does depend on E , $\phi \simeq \lambda_1^{-1} l^{3/2} \exp(-E) < \lambda_1^{-1} l^{-3} \ll 1$. See also the “phase” diagrams given in figure 1 (in $\phi - E$ space) and in figure 2 (in $E - \mu$ space). Note that “monomers” do occur in the polymerised phases (ii) and (iii), albeit only in very low concentrations. In the electron micrographs of Ref. [2], spherical micelles can indeed be seen in coexistence with long, polymerlike micelles.

One may infer from our calculations that the so-called sphere-to-rod transition could actually be a manifestation of the two transitions discussed above. This is plausible as the intermediate (ring) regime can be very narrow indeed for cylindrical assemblies which are quite rigid on the scale of a micelle diameter [12]. Even when the assemblies are not all that stiff, the ring regime may be difficult to detect as the worm-dominated phase sets in at very low volume fractions of order $l^{-5/2}$. Indeed, for fairly flexible linear micelles, such as those formed by the surfactant CPyBr in brine, we (conservatively) estimate that $l \simeq 4$, meaning that the worm phase must occur at a volume fraction of the order of 10^{-3} above the cmc. (Here l was equated to the ratio of the persistence length and the micelle diameter, which for this system are accurately known quantities [13].) Obviously, we are stretching the theory to the limit of its validity in this example, but it does once more confirm that rings should almost always be neglected in micellar systems [7].

Perhaps the most surprising conclusion of our analysis is that not only tight rings are suppressed, but also rod-like assemblies shorter than, say, a persistence length but longer than a few micelle diameters. The reason is that close to the rod limit very few bending modes remain that could, with the associated configurational entropy, help to compensate for the loss of translational entropy upon aggregation. It has to be noted that the *precise* impact of the freezing out of bending modes on the size distribution appears to be non-universal, i.e. it is model dependent. Indeed, other workers [14, 15, 16] do not find the relevant logarithmic terms in the single chain free energy at all. (In [14, 16] this is likely to be due to the approximate evaluation of $Z_1(N)$, and to the highly unusual choice of chain Hamiltonian in [15].) The question of how strongly our results depend on the choice of the rigid Gaussian chain model [9] needs to be addressed. This particular model exhibits “breathing” modes which are not present in the standard persistent or worm-like chain model [8], and could therefore exhibit spurious behaviour near the rod limit. It is, however, straightforward to verify that terms not identical but similar to those found in the rigid Gaussian chain model do arise in a continuous description of the (inextensible) worm-like chain model, when taking the limit $N \rightarrow \infty$, $l \rightarrow \infty$, $N/l \rightarrow 0$ [17]. (In this limit the problem can be treated at the level of a Gaussian fluctuation theory around the straight-rod configuration.) Again we find that the rod-like configurations in $\rho_1(N)$ are strongly suppressed, be it with a different prefactor of N^{-N} for $1 \ll N \ll l$. It is for this reason that we expect the general features of our “phase” diagram to be universal, at least in the limit $l \gg 1$.

Computer simulation studies of self-assembled lattice chains with a finite bending energy have recently appeared in the literature [18, 19, 20]. Unfortunately, comparison with our

predictions is not straightforward, for the chains interact strongly in the quoted works (and in fact exhibit order-disorder transitions) in contrast to the dilute case studied here. Ring formation is furthermore explicitly forbidden in [19, 20], where simulations were in addition restricted to two spatial dimensions only. (Another difficulty might arise from the rather low mean chain sizes of order ten investigated in [18, 19, 20].) Tentatively setting aside these reservations, some of the trends obtained from our analysis seem to be preserved in the simulations. Indeed, in [18] rings were found to play an insignificant role in the (“disordered”) worm-dominated phase, while in [19, 20] an increasing chain rigidity strongly reduces the mean aggregation number [21]. This happens, in our calculation, close to the (i) \rightarrow (iii) transition [17].

In conclusion, we have shown, using a simple mean-field analysis, that a finite chain rigidity may be the reason why ring formation is unimportant in many (if not all) micellar systems. As mean-field theory is thought to have a very broad range of validity in semi-flexible systems due to a combination of weak self-interactions and a narrow scaling regime [8], our results should be reasonably accurate all the way from the dilute to the concentrated regime, provided the system does not cross over to a liquid crystalline phase where a different behaviour has to be expected [18].

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